



From waste plastic to artificial lotus leaf: Upcycling waste polypropylene to superhydrophobic spheres with hierarchical micro/nanostructure

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ARTICLE INFO

Keywords:

Plastic upcycling
Polypropylene
Superhydrophobic
Microspheres

ABSTRACT

Polypropylene (PP) is the second most commonly used plastic in the industry and a key component in materials packaging and medical consumables. Its accumulation has increased due to the shift from reusable to single-use containers and the significant amounts of biomedical waste generated. We are working towards developing a cost-efficient methodology to convert polypropylene (PP) waste into superhydrophobic materials. Our approach involves the chemical treatment of waste PP to create micron-sized spheres (5 ~ 10 μm) with hierarchical nanostructures and superhydrophobic properties. The produced microspheres show a water contact angle up to 164° and a rolling off angle as low as 2.6°, comparable to natural lotus leaf. The effectiveness of this process has been demonstrated in waste PP from various sources, including surgical masks, syringes, take-away food boxes, and bubble tea cups. The resulting superhydrophobic material has promise for applications in superhydrophobic coating, self-cleaning, and water-oil separation.

1. Introduction

Mass production of plastics is accelerating rapidly due to the widespread use of plastic products in both industrial and consumer sectors after World War II. Most of the plastic products are disposable and end up as trash after a short period of use. Thus, approximately 70 % of all plastics ever produced (8.3 metric tons) have been discarded, of which 12 % have been burnt while 60 % have been put in landfills, and only 9 % have been recycled [1–4]. Incineration and landfill of waste plastics are apparently not viable solutions to our ecosystem. The incinerations of plastics resulted in emission of green-house gases and landfilled plastics could accumulate in natural environment for tens to hundreds of years which eventually contaminate natural resources. With increasing public awareness of plastic pollution, plastic recycling emerged as a more desirable solution, but it remains very challenging from both technological and economic standpoints. Plastic items produced from mechanically reprocessed plastics usually have reduced qualities due to the presence of impurities, cumulative polymer degradation, and the incompatibility between different types of plastics. As a result, only less than 1 % of plastics have been recycled for more than once [4]. Chemical recycling of plastics through processes such as pyrolysis [5–8] and depolymerization [9–12] is also limited by the requirement for high energy input and the lack of efficient methodologies.

Polypropylene (PP) is the second most commonly used plastic (next to polyethylene) in industry, with a market demand of approximately 60 metric tons in 2020 [13]. It has wide range of applications spanning from industrial to household settings and is utilized in sectors include packaging materials, medical disposables, textile, construction materials, and automotive components. Unfortunately, PP, with a recycling code of 5, is one of the least recycled post-consumer plastics [14–17]. Its accumulation is accelerating due to the global shift from reusable to single-use food and beverage containers, and huge amounts of biomedical wastes (e.g., surgical masks, syringes, and culture tubes) generated from clinics, hospitals, and personal protective measures.

Besides the “traditional” applications of polyolefin plastics, including PP, in manufacturing plastic products, there is also a growing interest in utilizing them as superhydrophobic coatings [18–24]. Superhydrophobic surfaces have numerous applications in the field of anti-corrosion, anti-icing, anti-fogging, self-cleaning, antifouling, oil-water separation, etc [25,26]. Analytical report shows that the global market for superhydrophobic coating might increase at an annual growth rate of 25.6 % from 2019 to 2024 and is projected to reach USD 2.7 ~ 4.2 billion by 2026 [25], indicating the increased demand and development in this sector. Superhydrophobic surfaces are normally fabricated by increasing the surface roughness or decreasing the surface energy of the materials [27,28]. There are several methods to produce

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<https://doi.org/10.1016/j.apcatb.2023.123378>

Received 16 June 2023; Received in revised form 4 September 2023; Accepted 7 October 2023

Available online 9 October 2023

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superhydrophobic surfaces from polyolefins, such as solution coating [18], doping with nanoparticles to increase the surface roughness [19, 20], molding from textured template [21,22], surface modification with perfluoro silane [23], and pulsed laser deposition [24]. These methods are usually tedious, difficult to control, or expensive. Therefore, developing practical feasible methods to fabricate superhydrophobic surfaces from polyolefins is of important significance.

Inspired by natural superhydrophobic surfaces such as lotus leaves, rose petals, rice leaves, and cicada wings, a number of biomimetic surfaces with similar micro/nanostructures are prepared [27–30]. For example, microspheres of block copolymer of polypropylene and poly (methyl methacrylate) (PP-PMMA) were synthesized by phase separation [31]. These microspheres have nano-scaled rough surface and show excellent superhydrophobicity with water contact angle up to 160° . Such polymer spheres with micro/nanostructures can also be produced on substrates by coatings with polypropylene solutions [32–35]. It was observed that the microspheres prepared from isotactic polypropylene could have rougher surface and better superhydrophobicity than that prepared from atactic polypropylene [32]. Moreover, using a mixed solvent of xylene and methyl ethyl ketone to dissolve polypropylene could yield a more hydrophobic coating than using a single solvent [34].

In this work, we developed a simple and cost-efficient methodology to convert waste polypropylene (PP) plastic into superhydrophobic materials (Scheme 1). Our approach includes the chemical treatment of waste PP to get partially oxidized polypropylene (OPP) followed by precipitation in a solvent to obtain OPP microspheres. The formation of the OPP microspheres doesn't rely on any substrate, different to that by coating methods [32–35]. All operations are performed under mild conditions and are scalable. The fabricated OPP spheres have hierarchical micro/nanostructures that resemble the papillae on lotus leaves in terms of size and morphology [29,30]. The coatings of the obtained OPP microspheres show good superhydrophobicity (water contact angle up to 160° and rolling angle as low as 3°), comparable to that of lotus leaves [29,30]. The process is compatible with presence of additives/impurities in PP plastics and is applicable for PP from various sources including medical disposables (e.g., surgical masks and syringes) and food containers (e.g., take-away food boxes and bubble tea cups). The potential applications of the product as a superhydrophobic material are demonstrated in the fields of superhydrophobic coating, self-cleaning, and water-oil separation. The outcome of this work demonstrates an advanced plastic upcycling technology and will aid to address the problem of plastic pollution and make valuable contributions to the circular economy.

2. Experimental

2.1. Materials and chemicals

Falcon® conical centrifuge tubes (15 mL or 45 mL) were used as polypropylene (PP) source in initial catalyst screening and reaction optimizations. When discarded tubes were used as PP source, they were cleaned with ethanol and water before use. The tubes were chopped into scraps (about $1\text{ cm} \times 1\text{ cm}$) for reactions. Benzyl chloride, trityl chloride and potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) are purchased from Sigma-Aldrich. Other chemicals and solvents not stated are purchased from Sigma-Aldrich.

2.2. Materials synthesis

A molten plastic method was used for polypropylene oxidation. About 2.0 g of PP scraps and 1 wt% of catalyst were loaded into a 20 mL open vial and heated at $180 \sim 300^\circ\text{C}$ for $1 \sim 12\text{ h}$ under stirring (300 rpm). At the reaction temperatures, typically 220°C , PP plastic was melted and therefore could be stirred. After the reaction, the partially oxidized polypropylene (OPP) was first dissolved in 2.5 mL of solvent-1, the mixture was then added to 20 mL of solvent-2 at room temperature where OPP microspheres were precipitated. The OPP microspheres were collected by filtration, washed with ethanol and dried at 80°C overnight under ambient conditions.

2.3. Materials characterizations

The SEM images were taken with a JEOL JSM 7500 scanning electron microscope. FT-IR spectra were collected on the PerkinElmer Spectrum 100 FT-IR Spectrometer. Water contact angles and rolling angles were determined using a DataPhysics TBU100 contact-angle measuring system under ambient conditions. Droplets ($3 \sim 6\text{ }\mu\text{L}$) of deionized water were placed on the samples using a micro-syringe. A minimum of five readings were taken from different positions of each sample. Thermogravimetric analysis was performed using PerkinElmer Pyris 1 TGA. Sample loading was 10 mg, heating rate was $10^\circ\text{C}/\text{min}$, air.

2.4. Testing for bacteria repelling

The testing was performed on $2.0 \times 2.5\text{ cm}$ substrates. About 1 mL of bacteria suspension ($1.0 \times 10^7\text{ CFU}$) of *Escherichia coli* (*E. coli*, ATCC No. 8739) or *Staphylococcus aureus* (*S. aureus*, ATCC No. 6538 P) was placed on the surface of each substrate. After 5 min of contact, the



Scheme 1. Upcycling of waste polypropylene plastic to superhydrophobic microspheres with particle size and hierarchical structures resemble that of papillae on the surface of lotus leaves.

substrates were tilted at 90° to allow the bacteria suspension to roll off. The substrates were rinsed with 5 mL of phosphate buffer solution (PBS). The rinsed solution was collected and gently mixed using vortex. Serial dilutions were made from the rinsed solution and were spread onto agar plates. Colonies counting was performed after 24 h incubation in a humidified incubator.

3. Results and discussion

3.1. The synthesis of OPP microspheres

Polypropylene is a non-polar compound, and it can hardly be dissolved in most organic solvents at room temperature. Our strategy is to partially oxidize polypropylene to alter its polarity, so that its solubility and crystallization behavior in solvent/nonsolvent would also change, making it possible to generate unique morphology from phase separation. The oxidation reaction was carried out by the “molten plastic method” in open vials without a solvent, air served as the oxidant, and free radical initiators were used as the catalysts. At the reaction temperatures, typically 220 °C, PP plastic was melted and therefore could be stirred. The catalysts generated free radicals under the high temperature conditions, activated molecular oxygen in air, and initiated the oxidation for C-H bonds of PP. The crude OPP was dissolved into a solvent then added into a non-solvent for OPP, and the microspheres with hierarchical micro/nanostructures were produced due to phase separation, similar to the precipitation behavior of the polar-nonpolar block copolymer [31].

An actual PP plastic product (Falcon® conical centrifuge tube) was used in our reactions as polypropylene (PP) source so that it can reflect the real-life application from waste PP materials. The crude OPP sample obtained from the oxidation step was dissolved in a less polar solvent like toluene (TL), and the solution was subsequently added to a more polar solvent like ethanol and water to precipitate OPP as microspheres

(5 ~ 10 μm) with hierarchical micro/nanostructures. These OPP microspheres resemble the papillae on lotus leaf and some other similar natural surfaces in terms of size and morphology, and these papillae are accepted to be the origin of superhydrophobicity on such natural surfaces [22,27,28]. Various free radical initiators were screened as catalysts to activate the inert C-H bonds of PP in the oxidation process. Among the various catalysts we have screened, reactions with benzyl chloride, trityl chloride and potassium persulphate gave good results in terms of sample morphology and superhydrophobicity properties (Fig. 1). Coatings from these OPP microspheres show water contact angles above 150°, which is a threshold for superhydrophobic surface. In contrast, pristine PP plastic with smooth surface shows a water contact angle of only about 100°.

FT-IR analysis was performed to investigate the oxidation of PP. As depicted in Fig. 2 A, the structures of OPP samples remained intact in comparison to pristine PP plastic; however, new absorbance attributable to carbonyl groups of oxygenated products appeared at around 1720 cm⁻¹ [36–38]. After base treatment of the OPP sample, new absorbance assignable to carboxylate ions appeared at 1542 cm⁻¹ [39, 40], indicating the carbonyl groups could be in the forms of ketone, aldehyde, and carboxylic acid (Fig. 2B). The extent of oxidation in the first step of reaction is crucial for getting the OPP microspheres in the subsequent precipitation step. It appears that potassium persulphate is a stronger catalyst than benzyl chloride and trityl chloride in terms of the absorbance at 1720 cm⁻¹. The easier cleavage of the -O-O- bond in K₂S₂O₈ can generate strong sulfate anion free radicals (SO₄^{•-}) which initiate the oxidation reaction for PP [41,42]. With 1 wt% loading amount of potassium persulphate, 6 h oxidation at 220 °C is sufficient to get the OPP microspheres from the next precipitation step (Fig. 1D). However, when reactions are carried out with benzyl chloride and trityl chloride as catalysts at the same loading amount respectively, 12 h oxidation at 220 °C is required (Fig. 1A & B); while a shorter reaction time leads to more undesired irregular particles in the final OPP product

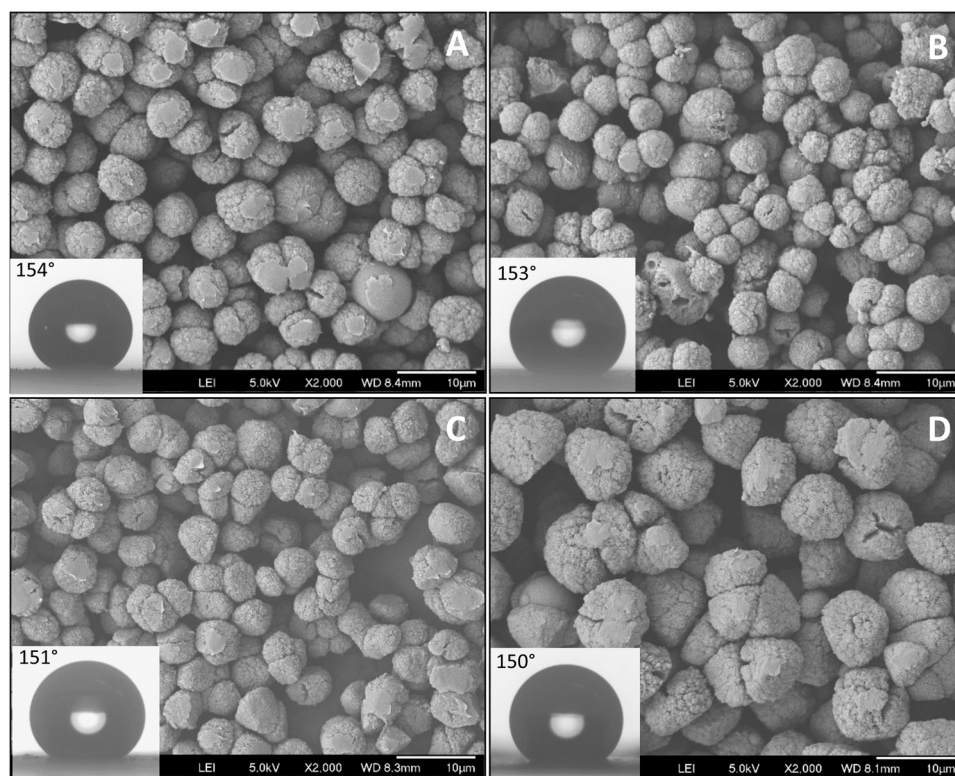


Fig. 1. SEM images of OPP microspheres synthesized with different catalysts. A) benzyl chloride; B) trityl chloride; C) potassium persulphate; D) benzyl chloride plus potassium persulphate catalysts (1:1). Reaction conditions: PP 2.0 g, catalyst 1 wt%, 220 °C 12 h for A & B, D, 220 °C 6 h for C. Crude OPP dissolved in toluene and precipitated in ethanol.

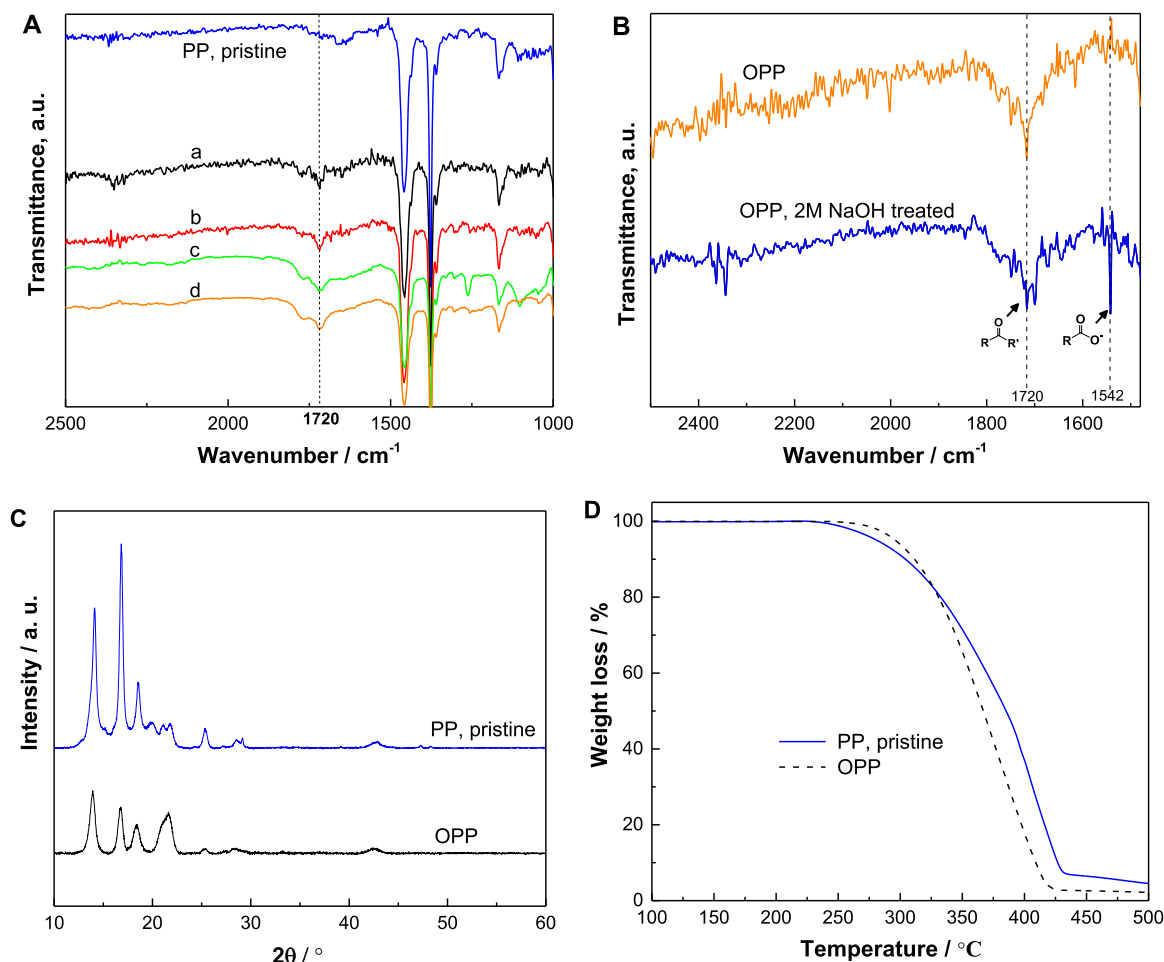


Fig. 2. (A) FT-IR profiles of OPP synthesized from different oxidations. PP 2.0 g, catalyst 1 wt%, 220 $^\circ\text{C}$ 12 h for a, b & d, 220 $^\circ\text{C}$ 6 h for c. Catalysts for samples: (a) benzyl chloride; (b) trityl chloride; (c) potassium persulphate; (d) a combination of benzyl chloride and potassium persulphate in 1:1 ratio. (B) FT-IR profiles of OPP sample (a) before and after treated with 2 M NaOH for 16 h at room temperature. (C) XRD patterns of PP and OPP sample (c). (D) Thermal gravity analysis for PP and OPP sample (c). Sample loading 10 mg, heating rate 10 $^\circ\text{C}/\text{min}$, air.

from precipitation (Fig. S1). Moreover, potassium persulphate is safer in handling and more environmentally friendly than benzyl chloride and trityl chloride. To better understand the influences of surface functional groups on the hydrophobicity, we did the reduction for a crude OPP sample, which was just collected after oxidation, without the next precipitation step. Thus, this crude OPP doesn't have the unique micro/nano-structures as OPP microspheres and therefore has a smaller water contact angle than the latter sample. Detailed data of water contact angles for crude OPP before and after reduction are provided in Table S1. It turned out that after reduction the water contact angle for crude OPP decreased to 86 $^\circ$, smaller than the values of pristine PP plastic (100 $^\circ$) and crude OPP before reduction (121 $^\circ$). This is because the surface functional groups are reduced to hydroxyl and induced the strong hydrogen bonding. These results also verify the superhydrophobicity of OPP microspheres relies on the unique micro/nano-structures.

The X-ray diffraction pattern of the OPP microspheres is almost the same as pristine PP plastic (Fig. 2 C), indicating that the structure of OPP was basically retained after oxidation treatment followed by precipitation. However, the crystallinity of OPP is lower than that of pristine PP in terms of the diffraction intensity. Thermal gravity analysis shows that OPP is as stable as pristine PP in air as no significant difference in weight loss percentage was observed between the two (Fig. 2D). In general, the physical properties of OPP did not change remarkably after partially functionalized through the oxidation reaction.

One problem with our microspheres synthesis is that irregular particles or big agglomerations were observed in samples precipitated from

toluene (TL) as the first solvent and ethanol as the second solvent (Fig. 3A). Modifications such as changing the concentration of OPP in TL, the rate of addition into ethanol, and stirring speed were not able to eliminate such agglomerations. However, by selecting appropriate combinations of solvents for the precipitation, uniform and dispersed microspheres could be obtained from reactions with various catalysts. A combination of a less polar solvent (such as toluene) to dissolve OPP and a more polar solvent (such as water) for the subsequent precipitation is effective in achieving dispersed OPP microspheres of around 2 ~ 10 μm (Fig. 3B-C). Additionally, the combination of two organic solvents like methyl isobutyl ketone (MIBK) and ethanol for the two separate steps also showed promising results in getting uniform spheres of about 5 μm (Fig. 3D). The combinations of a solvent and a nonsolvent can also be used for PP coatings [34]. It was found that using a mixed solvent of xylene (a solvent) and methyl ethyl ketone (a nonsolvent) to dissolve polypropylene could yield a more hydrophobic coating than using a single solvent. The nonsolvent might facilitate polymer precipitation by phase separation.

After determining the appropriate catalyst for oxidation and the suitable solvents for precipitation, other contributing factors in the reaction such as reaction temperature, reaction time, and amount of catalyst loading were studied. A reaction temperature above 220 $^\circ\text{C}$ is preferred because the use of a higher temperature allows reducing the viscosity of melted PP, thus achieving greater homogeneity and improving reaction kinetic. Additionally, with a higher catalyst loading of 2 %, OPP microspheres could be synthesized in 3 h at 220 $^\circ\text{C}$

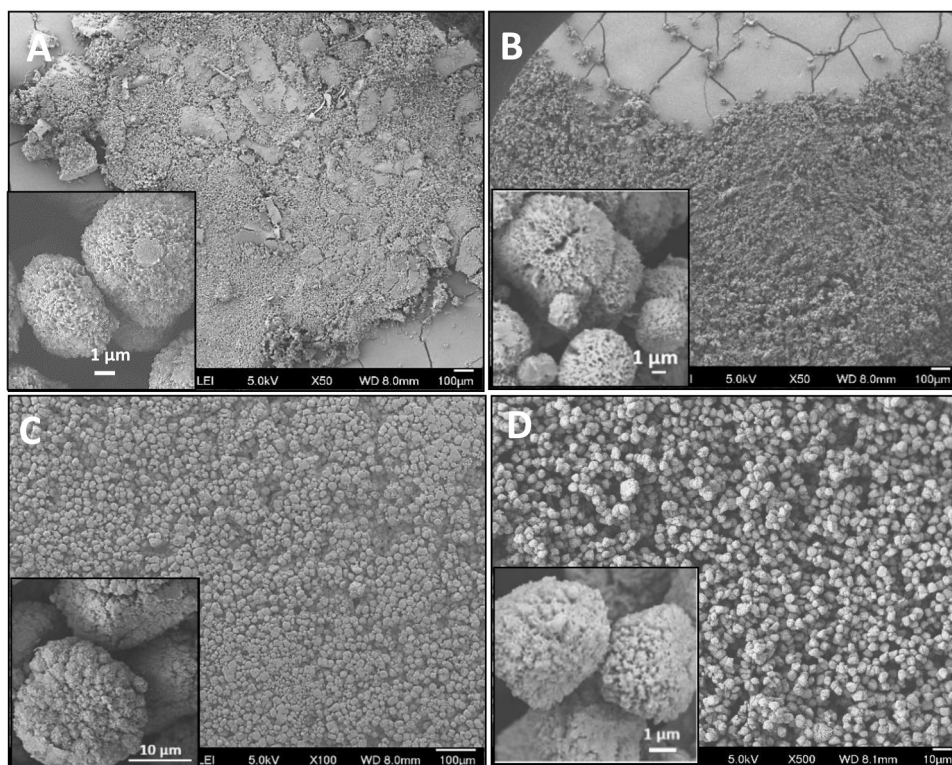


Fig. 3. SEM images of OPP microspheres synthesized under different conditions. A) PP 2.0 g, $K_2S_2O_8$ 1 wt%, 220 °C 6 h. Toluene (TL) and ethanol for precipitation; B) PP 2.0 g, $K_2S_2O_8$ 1 wt%, 220 °C 6 h. TL and water for precipitation; C) PP 2.0 g, benzylchloride 1 wt%, 220 °C 12 h. TL and water for precipitation; D) PP 2.0 g, $K_2S_2O_8$ 1 wt%, 220 °C 6 h. MIBK and ethanol for precipitation.

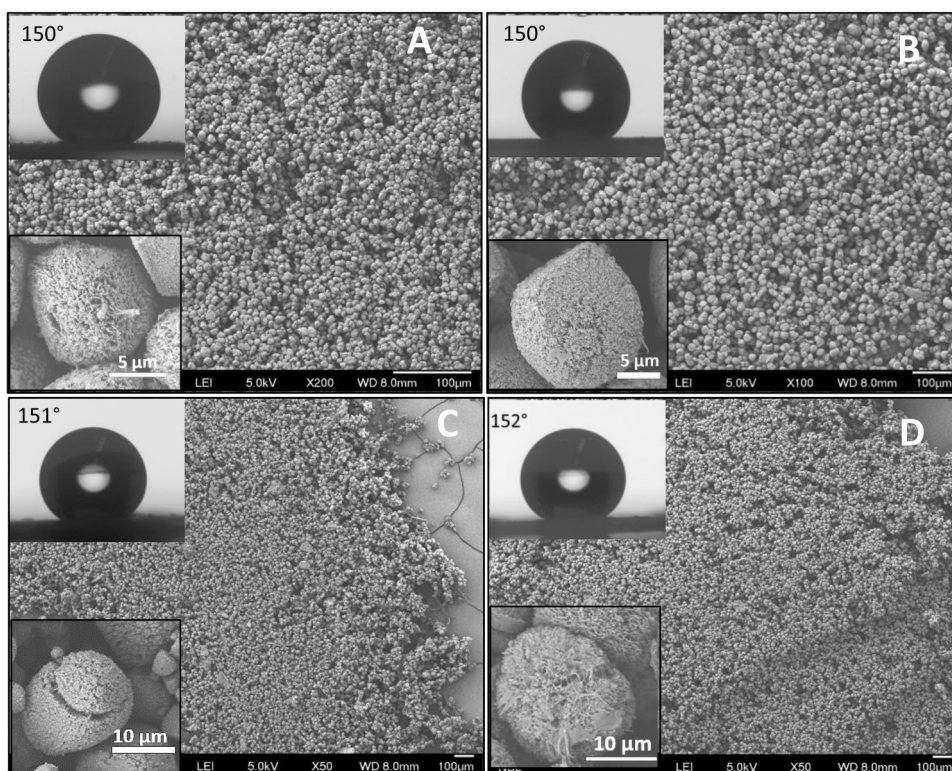


Fig. 4. SEM images of OPP microspheres synthesized under different conditions. A) PP 2.0 g, $K_2S_2O_8$ 2 wt%, 220 °C 3 h. B) PP 2.0 g, $K_2S_2O_8$ 1 wt%, 250 °C 1 h. C) PP 2.0 g, $K_2S_2O_8$ 5 wt%, 300 °C 30 min. D) PP 2.0 g, $K_2S_2O_8$ 5 wt%, 300 °C 15 min. TL and water solvents for precipitation.

(Fig. 4A). At even higher reaction temperatures and/or higher catalyst loadings, OPP microspheres could be synthesized in much shorter reaction time. For example, uniform microspheres were obtained in 1 h at 250 °C with 1 % of catalyst loading (Fig. 4B), or in 15 ~ 30 min at 300 °C with 5 % of catalyst loading (Fig. 4C & D). The broad range of reaction conditions available for the oxidation step make this reaction very flexible for practical application.

Polypropylene can be categorized into atactic PP, syndiotactic PP, and isotactic PP in terms of different alignments of the methyl groups. PP with different structures may display different physical properties such as variation in their crystallinity and melting point. For example, isotactic PP is crystalline with a melting point of up to 160 °C, while atactic PP is amorphous with a melting point of 60 ~ 80 °C. As a result of the predominant presence of isotactic polypropylene in commercial PP products (> 70 %, with the rest being atactic PP and small amount of additives), pure isotactic and atactic PP were used separately as starting materials for OPP spheres synthesis to enable a better understanding of the reaction. It turned out that the OPP sample synthesized from pure isotactic PP (Fig. S2) is very similar to that synthesized from a commercial PP plastic (e.g., Falcon® conical centrifuge tube) in terms of morphology and superhydrophobicity. However, the OPP sample synthesized from pure atactic PP agglomerated in the precipitation step and the nanostructure on surface was also not achieved (Fig. S3).

The actual compositions of PP vary with PP products; moreover, different types of PP products may have different additives such as stabilizers and antioxidants. To verify the feasibility of our protocol across a wider range of commercial PP sources, we applied the optimized synthesis conditions to PP from various sources including takeaway boxes, bubble tea cups, measuring cups, and non-woven surgical masks. As shown from Fig. 5A-E, all OPP samples synthesized from other PP sources are in uniform micron-sized spheres with nanostructures on surface. This indicates that the reaction is not hindered by the presences

of different stabilizers and antioxidants in PP, and the protocol can be applied to the upcycling of waste PP plastics from a wide range of sources. Another 20 g scale reaction was also conducted for PP from centrifuge tubes as a source to verify the scalability of the reaction (Fig. 5F). Notably, OPP microspheres with a yield of above 95 % were obtained after precipitation. The sample from this larger scale reaction showed similar morphology and superhydrophobicity (water contact angle of 158°) as the ones from smaller scale reactions.

3.2. The superhydrophobicity of OPP microspheres

To understand the underlying phenomena responsible for the superhydrophobicity, a step-by-step interaction of the water droplet with the OPP coated superhydrophobic surface was studied with the results depicted in Fig. S4. A water droplet with volume of 3 μL ~ 10 μL was dripped from a micro glass syringe (Fig. S4A), and the OPP coated substrate was lifted to allow contact with the water droplet (Fig. S4B). When the OPP substrate was further lifted slightly, the water droplet was pressed but repelled by the OPP surface (Fig. S4C). When the substrate was lowered down, the water droplet would detach or remain attached to the micro syringe, depending on the volume size of the water droplet. When the water droplet volume was 3 μL , it was wholly repelled from the OPP surface and moved back/returned to the micropipette (Fig. S4E). When the water droplet volume was 6 μL , the droplet will most likely revert to the micropipette with only occasional adhesion to the OPP surface. Only when the volume of water droplet was increased to 10 μL or larger, the droplet primarily attached to the substrate because of the additional gravity (Fig. S4F). As such, we proceed with water droplets of 6 μL as a standard to measure the contact angles of the superhydrophobic OPP spheres in our experiments.

Water contact angle and rolling angle are important parameters for deciding the applications of superhydrophobic materials [22,27,28]. We

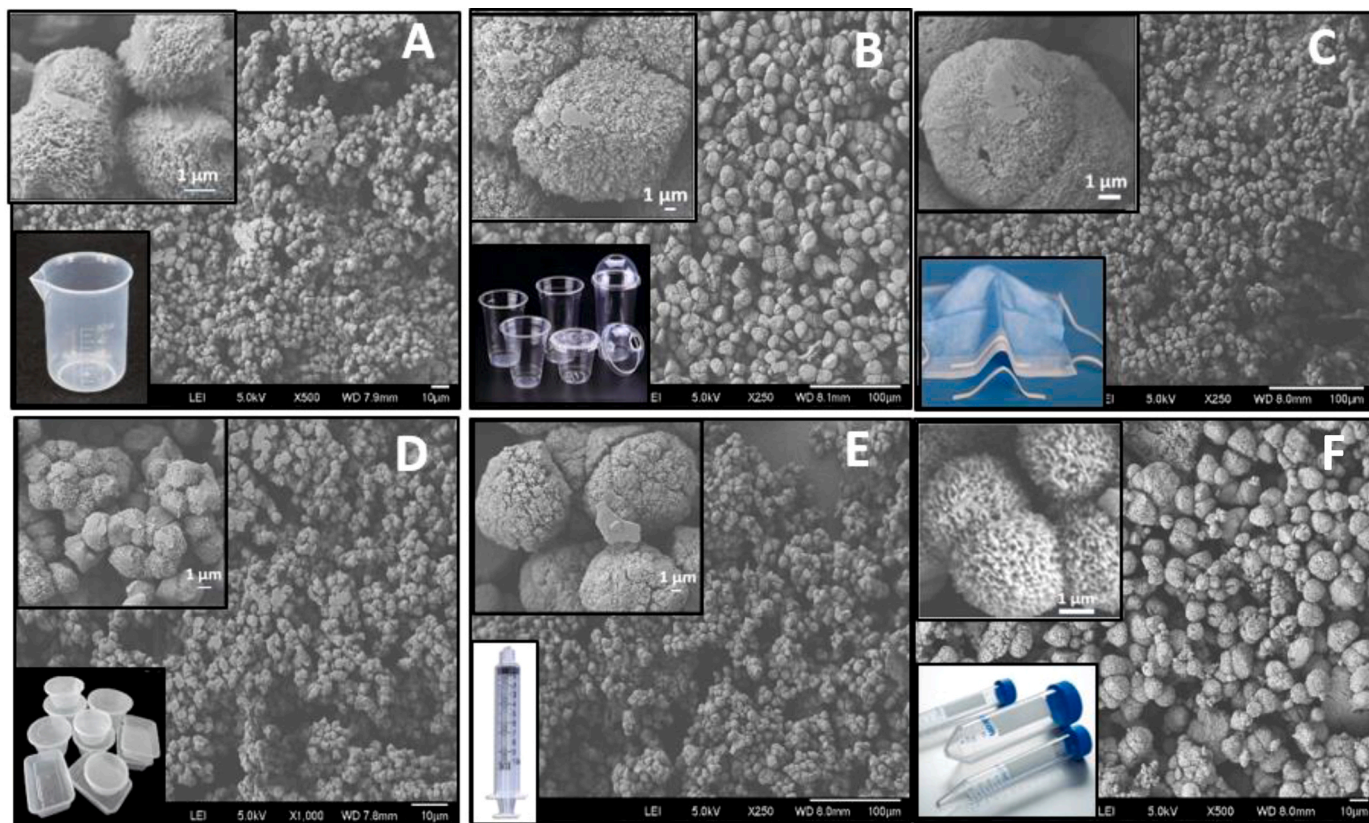


Fig. 5. SEM images of OPP microspheres synthesized from different sources. Reaction conditions: $\text{K}_2\text{S}_2\text{O}_8$ 1 wt%, 220 °C 6 h. PP loadings in reactions: A-E, 2.0 g, F, 20 g. TL and water are used for precipitation.

also used a 75 μm sieve to break down any possible agglomerations of the dried powder sample of OPP microspheres (as in Fig. 1C). After passing through the sieve, the collected OPP microspheres are more dispersed. A water contact angle of 164° was measured (Fig. 6A) for the sieved OPP microspheres. The sample also showed very low adhesion to water. The water droplet completely rolled off at a tilt angle below 5° and a rolling angle of 2.6° was recorded (Fig. 6B). To give a vivid demonstration of how superhydrophobic the sample is, water dyed with different colors were deposited onto the surface of an OPP coating (Fig. 6C). All the colored water droplets are round because of the excellent repellence of the surface. The excellent superhydrophobicity of this OPP coating is comparable to the natural lotus leaf which usually displays a water contact angle of about 160° and a rolling angle of about 3° (Fig. 6D). Concerning the practical potential of superhydrophobic coatings, commercial powder coatings are formulated with adhesives to ensure sufficient binding between the spheres and the substrates. To demonstrate the potential for real application, a mixture of 10 wt% OPP spheres in polyurethane/THF solution (1: 60) was brushed onto a glass substrate, a smooth coating with a water contact angle of 153° was

obtained (Fig. 6E). The interparticle bindings provided by polyurethane adhesive could be clearly observed from Fig. 6F, indicating good compatibility of OPP with the adhesive. The excellent superhydrophobicity of OPP spheres signifies its potential applications in fields like superhydrophobic coating, self-cleaning and water-oil separation.

3.3. Self-cleaning ability of OPP microspheres coated surface

A superhydrophobic surface with low adhesion to water has self-cleaning function because of the anti-fouling and anti-bacterial abilities [43]. The anti-bacteria properties of water-repellent surfaces with OPP coating were evaluated. The testing was performed on equally sized substrates with/without OPP coatings using both gram-negative *Escherichia coli* (*E. coli*) and gram-positive *Staphylococcus aureus* (*S. aureus*). About 1 mL of bacteria suspension (1.0×10^7 CFU/mL) was placed on the surface of each substrate. After 5 min, the substrates were tilted at 90° to allow the bacteria solution to roll off. Subsequently, the substrates were rinsed with 5 mL of phosphate buffer solution (PBS).

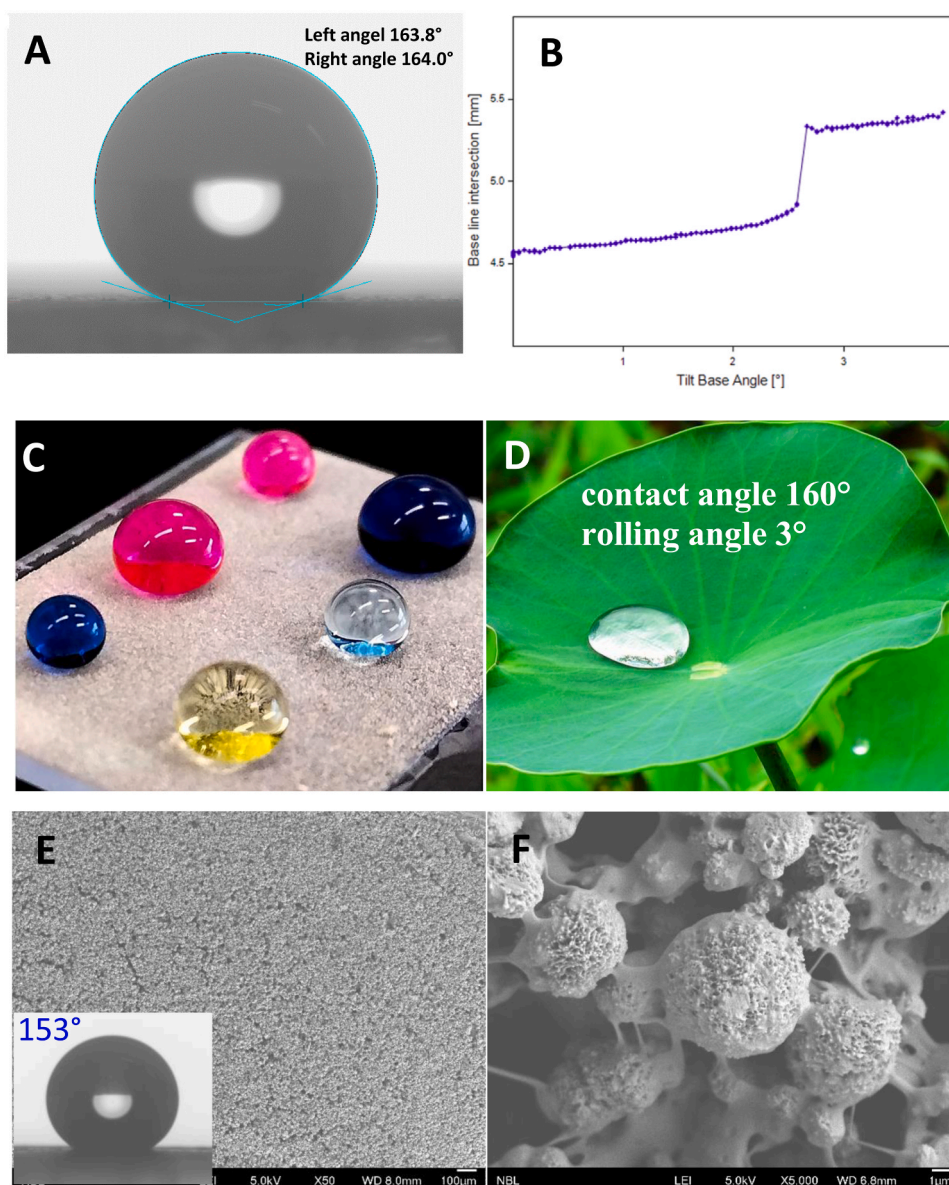


Fig. 6. (A) The water contact angle of an OPP coated surface. (B) The rolling angle of an OPP coated surface. (C) Dye colored water drops on an OPP coating. (D) Natural lotus leaf. (E) & (F) Formulated coatings with polyurethane as an adhesive. Formulation: 10 wt% OPP microspheres in polyurethane/THF solution (1: 60).

The rinsed solution was collected and gently mixed using vortex. The rinsed bacteria solution was then diluted appropriately and spread onto agar plates for colony counting. After 24 h of incubation in a humidified incubator, colonies counting was performed. The values of colony formation unit (CFU) from different substrate surfaces were summarized in Table 1 to compare the ability in bacteria repelling.

With the smooth PP surface as a control substrate, the OPP coated substrates showed more than 99 % reduction rates for both *E. coli* and *S. aureus*. The results revealed excellent bacteria repelling ability of OPP coated substrates against both gram-negative and gram-positive bacteria, in contrast with other superhydrophobic surfaces that selectively repel certain types of bacteria [44]. The homogeneity at bacteria scale of the OPP coated surface may enable low bacteria adhesion [45]. Because bacteria do not stick to the superhydrophobic OPP surface and remain in the solution, they will roll off with the water droplet and achieve self-cleaning.

3.4. Superhydrophobic coating with crude OPP

Besides utilizing OPP spheres as superhydrophobic coatings, we discovered that crude OPP in a toluene solution can be directly used for creating superhydrophobic coatings. In our experiments, we submerged a hydrophilic fabric, with capability of absorbing water entirely (water contact angle is zero), into an OPP/TL solution (30 mg/mL) for approximately one minute. Subsequently, we allowed the fabric to dry overnight at 80 °C. This treatment did not noticeably alter the color or overall appearance of the fabric. However, it rendered the fabric with water repellent ability, evidenced by a significantly higher water contact angle of 154° (Fig. 7A). This outcome indicated a transformation of the fabric's nature from hydrophilic to superhydrophobic after the crude OPP solution treatment. Further analysis using scanning electron microscopy (SEM) revealed that OPP microspheres were uniformly attached on the fabric's fibres (Fig. 7B-D). These OPP microspheres exhibited similar hierarchical micro/nano structures as those synthesized through precipitation. It is plausible that OPP can undergo crystallization either in a non-solvent (as demonstrated by our precipitation method using water) or through rapid solvent evaporation. The direct coating approach using the OPP/TL solution offers practical advantages in terms of its implementation and could serve as a complementary method to coating with OPP spheres.

3.5. Water-oil separation by OPP microspheres

Frequent oil spills not only pose a significant threat to our ecosystem by causing pollution but also result in the wastage of valuable sources that could be used for chemicals and fuels. Thus, it is very important to

develop efforts for collection and re-utilization of spilled oil. In relation to water-oil separation, some superhydrophobic foams could be used for the selective absorption of oil from spills [46,47]. However, a dynamic water-oil separation is preferred for higher efficiency [48,49]. As our oxidized polypropylene microspheres are oleophilic (absorbs oil) but hydrophobic (water repellent), it is therefore utilized in an attempt to achieve dynamic water-oil separation. Fig. 8A illustrates the setup for the continuous removal of artificial oil spill (hexane) from water. The real setup for this experiment is shown in Fig. S4A. Water was red colored with Rhodamine B for easier differentiation with the hexane phase. The separator was adapted from a gas distributor of a bubbler. The OPP microspheres were packed in the sintered glass and placed at the interface of hexane/water, viz, half of the OPP packed separator was dipped in water and the other half remained in hexane, allowing hexane and water to pass through the OPP packing selectively or simultaneously. A vacuum pump was connected to the oil collector to provide additional driving force for the separation. When the pump was powered on, only hexane was absorbed by OPP and moved continuously to the collection bottle while the red dyed water was not absorbed at all (Fig. S5C). The selective separation of hexane is due to the superhydrophobic and superoleophilic nature of the OPP spheres. The same setup was also used for the separation of a more polar solvent such as chloroform from Rhodamine B colored water (Fig. S5D). Due to its higher density than water, chloroform forms the bottom layer of the mixture. Despite being heavier than water, chloroform was able to be selectively separated by the OPP packed separator when the vacuum pump was powered on (Fig. S5D), showing strong absorption of chloroform and repulsion of water. Chloroform was collected continuously (Fig. S5E), similar to the case of hexane separation. As the OPP microspheres display good absorption for both nonpolar and polar organic solvents, it would be a useful material for addressing small-scale light oil spills.

4. Conclusion

A simple and scalable methodology is developed for the upcycling of polypropylene (PP) plastic into superhydrophobic materials. Our approach includes the chemical treatment of waste PP into partially oxidized polypropylene (OPP), followed by precipitation in a solvent to produce micron-sized spheres with hierarchical nanostructures and superhydrophobic property. Aspects such as the catalysts, reaction conditions and solvents used for synthesis were investigated. The process is successfully demonstrated using polypropylene plastic from various sources such as surgical masks, syringes, take-away food boxes, and bubble tea cups. The OPP microspheres coated surface shows excellent water repellence and displays a water contact angle up to 164° and a rolling angle of about 3°. The superhydrophobicity of this OPP coating is comparable to that of natural lotus leaf which usually displays a water contact angle of about 160° and a rolling angle of about 3°. The potential applications of the product as a superhydrophobic material are also demonstrated for self-cleaning and water-oil separation. Compared to the smooth PP surface used as a control substrate, the OPP coated substrates showed more than 99 % reduction rates in adhesion of both gram-negative *E. coli* and gram-positive *S. aureus*. Dynamic oil-water separation capability of OPP microspheres was also successfully demonstrated with artificial oil spills made from hexane/water or chloroform/water. The OPP microspheres display good absorption for both nonpolar hexane and polar chloroform, signifying its potential application for the cleaning of small light oil spills.

CRediT authorship contribution statement

Xiukai Li: Conceptualization, data collection and analysis, manuscript writing. **Jinquan Wang:** data collection, manuscript writing. **Guangshun Yi:** data collection, manuscript writing. **Siew Ping Teong:** data collection, manuscript writing. **Shook Pui Chan:** data collection,

Table 1
Bacteria repelling test for OPP coated substrates.

Substrate	EC (-)		SA (+)	
	No. of CFU	Reduction Rate	No. of CFU	Reduction Rate
PP	1.21 × 10 ⁵ 1.30 × 10 ⁵ 1.25 × 10 ⁵ (average)		5.08 × 10 ⁴ 5.04 × 10 ⁴ 5.06 × 10 ⁴ (average)	
OPP-1	40 30 35 (average)	99.97 %	35 25 30 (average)	99.94 %
OPP-2	35 25 30 (average)	99.98 %	190 160 175 (average)	99.65 %

Substrate size 2.0 × 2.5 cm; bacteria solution 1 mL, 1.0 × 10⁷ CFU/mL; contact time 5 min; tilt angle 90°. OPP-1 is the sample shown in Fig. 3 D, OPP-2 is the sample shown in Fig. 3 B. Coating thickness ~ 160 μm. EC (-): *E. coli*; SA (+): *S. aureus*.

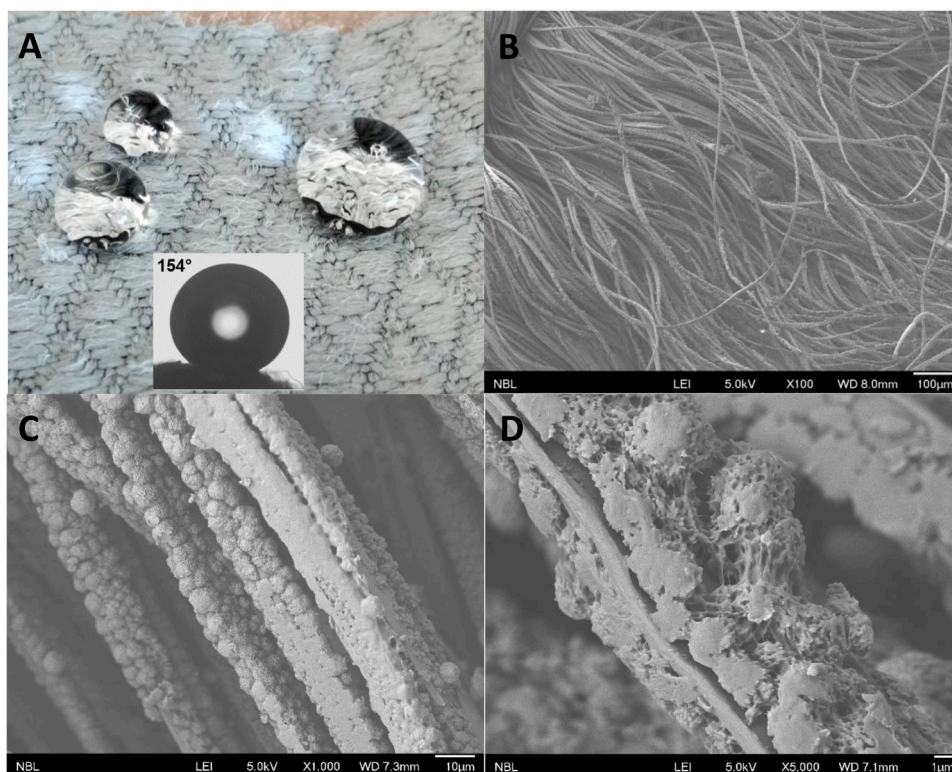


Fig. 7. Superhydrophobic fabric fabricated by dip coating a hydrophilic fabric with OPP/TL solution (30 mg/mL). (A) Water droplets on OPP coated fabric. (B)-(D) SEM images showing OPP spheres attached on the fibres of the fabric.

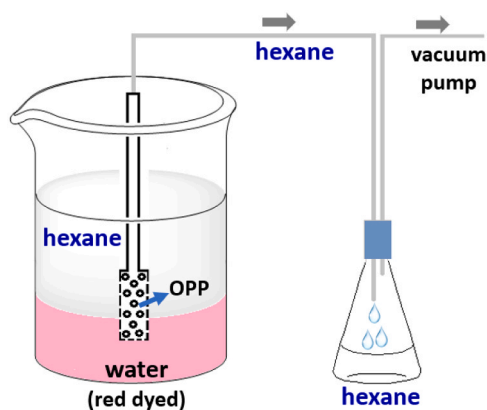


Fig. 8. The setup for the dynamic water-oil separation.

manuscript writing. **Yugen Zhang:** Conceptualization, manuscript writing, discussion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work is supported by Agency for Science, Technology and

Research (A*STAR), Singapore.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123378](https://doi.org/10.1016/j.apcatb.2023.123378).

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